

# **PARTITIONING OF Re, Os, AND Ir BETWEEN METAL AND SILICATE LIQUID.**

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We have employed a variety of experimental and analytical techniques to investigate the geochemistry of Re and other highly siderophile elements. Frankly, these investigations have met with only limited success, but we report our preliminary results to emphasize the difficulty of precisely determining the solubility of highly siderophile elements in silicate liquids [e.g., 1].

**Experimental.** Three types of experimental designs have been employed. (i) Sealed silica tubes at one bar. This was the same design and glass composition as that of Jones and Drake [2]. The metal-sulfide-silicate system is self-buffered, with  $f_{O_2}$  (~IW to ~QFM) determined by changing the Fe/Ni ratio of the metal [3]. These experiments were simultaneously spiked with ~0.75 wt.% each of Re, Os and Ir. Temperature was either 1250 or 1350°C. Initial silicate composition was that of a eucrite basalt [2] (ii) Silicate samples run on Re loops at one bar. In these experiments the metal phase was pure Re, so silicate Re concentrations represent solubility limits. The  $f_{O_2}$  was controlled by flowing CO-CO<sub>2</sub> to be QFM-1. At higher  $f_{O_2}$ 's the Re loop reacts to form volatile Re oxides. Runs were performed below the liquidus (1260°C), so olivine was also present. Silicate composition was a primitive shergottite (Eg1; [4]). (iii) Graphite capsule experiments at 10 kbar. The  $f_{O_2}$  of these experiments is controlled by C-CO<sub>2</sub> equilibria and is between IW and QFM. These experiments were spiked with pure Os and pure Re as the only metal phases. No alloying of these metals was observed. Therefore, silicate Os and Re concentrations should represent solubility limits. Runs were performed below the liquidus, so either pyroxene (Eg1) or olivine (high-pressure MORB analog MO695 from J. Longhi) was present.

**Analytical.** All noble siderophile abundances were too low to measure with the electron microprobe, so other techniques were employed. (i) Micro-INAA. Aliquots of the sealed silica tube glasses were analyzed for Ir by micro-INAA at JSC. Some of these results have already been presented [5]. The heterogeneity of Ir in these samples made it likely that true solubility was not measured and that Ir was present as suspended nuggets [5]. (ii) Ion Microprobe. The 10 kbar glasses were analyzed by ion probe using the Edinburgh Cameca 4f and standard energy-filtering techniques. No Re or Os was present above detection levels.

Estimates of upper limits to Os concentrations in glass ranged from 50 to 250 ppb, based on an ion yield from pure Os metal of >0.05. An upper limit for Re is subjectively given as <<1 ppm. Upper limits for Re and Os in olivine and pyroxene crystals are lower still. (iii) Laser-ablation ICPMS. Glass and olivine from the Re loop experiments were analyzed by laser-ablation ICPMS [6]. Re was below detection limit in olivine but is definitely measurable in the glass. However, like Ir in the sealed silica tube experiments, Re in the glass is highly variable (factor of 10-100) on a 1-10 $\mu$  scale, again suggesting the presence of nuggets. An even more troubling aspect of these analyses is that, occasionally, the Re signal drops to background levels — a problem we have not encountered in analyses of our standard glass (NIST610). Thus, despite a general consistency between analyses of different areas, it is possible that nuggets are largely responsible for the Re signal. Alternatively, there could be volatile loss of Re from the silicate, with resulting heterogeneities. A complex sequence of volatile loss and subsequent replenishment by dissolution of the loop (or the nuggets) is also a possibility. (iv) Isotope Dilution; Thermal Ionization Mass Spectrometry. Larger aliquots of the glasses analyzed by micro-INAA (sealed silica tube experiments) were analyzed for Re and/or Os by isotope dilution. The variability of the Ir analyses on much smaller aliquots suggests that Re and Os may also be affected by suspended nuggets but bulk analysis does not allow us to evaluate this possibility directly.

**Discussion.** (i) Henry's law. In some instances, where we have used pure Re and/or Os as the metal phase, we are clearly not in the Henry's law region for the metal phase, although knowledge of activity-composition relationships could be used to correct for this [7]. A potentially more serious problem is our use of several tracers in the sealed silica tube experiments. However, our new  $D_{Ir}$  measurements for solid metal/liquid metal [8] agree extremely well with those measured with fewer tracers [9], suggesting that Henry's law is obeyed in the metallic system for those experiments. Henry's law evaluation for the silicate is more difficult, but, at the ppb level, this is presumably not a concern. (ii) Heterogeneity. Silicate glasses from our sealed silica tube experiments are clearly heterogeneous in their Ir contents, as are glasses from experiments run on Re loops. Under the assumption that larger Ir and Re

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contents reflect nuggets, as opposed to true solution, our only recourse is to use our lowest concentrations to calculate minimum partition coefficients. For Os and Ir, minimum  $D$ 's for solid metal/silicate liquid are comparable and hover in the vicinity of  $10^7$ . However, as we and others have emphasized, the true value may be much larger [5, 7]. For Re,  $D$  values are slightly lower,  $10^5$ - $10^6$ . But it should also be noted that these Re  $D$ 's are still higher than those reported by Drake and Jones at comparable  $f_{O_2}$ 's [10]. (iii) Measurable difference between Re and Os? Despite the difficulties of demonstrating true equilibrium, there appear to be real differences between Re and Os partitioning. Currently, we only have one sample for which we have measured both Re and Os from the same aliquot of glass. For this sample,  $D_{Os}$  is a factor of four greater than  $D_{Re}$ . This difference is well outside analytical precision, but the experimental reproducibility is not yet known. More data are needed to evaluate the degree to which Re and Os fractionate. (iv) Low levels of Re compared to expectation. We have been extremely disappointed over our inability to measure Re or Os in our 10 kbar experiments. For Re the disappointment was acute. The  $f_{O_2}$  of these high pressure experiments is significantly above IW. And, based on the systematics of Re solubility presented by O'Neill et al. [7], we predicted that we should have tens of ppm Re in our silicate liquid, an amount that should be measurable by ion probe. Our failure to detect Re in these experiments presumably means either that the ionization efficiency of Re in silicate matrices is extremely low or that the solubility limits determined by [7] are much higher than in our experiments. We intend to subject these charges to the laser ablation ICPMS technique to see if improvements in detection limit can be achieved. The "success" of the analyses of the Re-loop experiments suggests that this may be a profitable avenue to explore. If the Re signal from the glass of the Re loop experiment really represents dissolved Re, then the Re concentration of the glass is ~26 ppm, broadly consistent with the results of [7]. (v) Olivine/liquid partitioning of Re. Despite the difficulties associated with these analyses, if we take our least variable glass and olivine Re analyses as most reliable, we calculate the 3 $\sigma$  upper limit for  $D_{Re}$  olivine/liquid to be 0.03. Thus, Re appears highly incompatible in olivine at QFM-1. However, we recommend caution in this interpretation, as we are still trying to understand the variability of our Re signal. (vi) Comparison of measured and predicted Re

partition coefficients. Righter and Drake [11] have presented a regression equation for predicting  $D_{Re}$  metal/silicate liquid that takes into account changes in temperature, pressure, oxygen fugacity, and bulk composition. For two of our new sealed silica tube experiments, we can directly compare our measured partition coefficients to those predicted by [11]. Even if Re nuggets were present in the glasses of these experiments, they should still represent lower limits to the true partition coefficient. The agreement between measurement and prediction is mixed. At higher temperature and higher  $f_{O_2}$  (1350°C;  $\log f_{O_2} = -9.7$ ), the agreement is reasonably good; the measured  $D_{Re}$  solid metal/silicate liquid is  $5.1 \times 10^5$  and the calculated value is  $1.4 \times 10^6$ . However, at lower temperature and lower  $f_{O_2}$  (1250°C;  $\log f_{O_2} = -12.3$ ), the measured  $D_{Re}$  solid metal/silicate liquid is  $5.5 \times 10^6$ , whereas the predicted value is  $4 \times 10^4$ . The reason for the discrepancy is most likely that our new Re partition coefficients are larger than those of [10], which were used to constrain the regression of [11]. Because of the many uncertainties that we have described here, we suggest that modeling of core formation based on Re systematics [e.g., 11] is premature. Even so, at this juncture we have no reason to assume that metal/silicate partitioning will preserve a chondritic  $^{187}\text{Re}/^{188}\text{Os}$  ratio. Consequently, we believe that the near-chondritic  $^{187}\text{Os}/^{188}\text{Os}$  ratios observed in fertile spinel lherzolites [12] are best explained by a late veneer.

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